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Formulation and Make-Up of Simulated Concentrated Water, High Ionic Content Aqueous Solution

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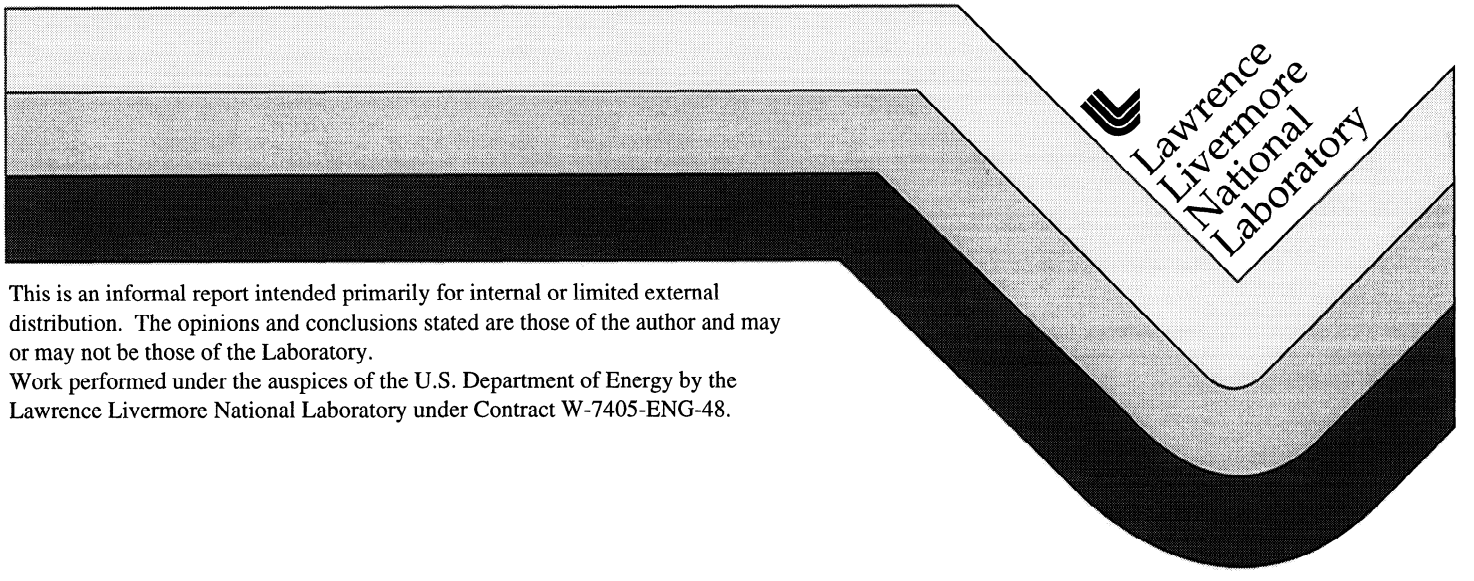
April 4, 1997



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University of California

Lawrence Livermore National Laboratory

YUCCA MOUNTAIN PROJECT

Technical Implementing Procedure

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Page:	1 of 7

Subject: Formulation and Make-Up of Simulated Concentrated Water, High Ionic Content Aqueous Solution

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Training Required: Yes ■ No ☐

Comments: Addition of balance to acceptable list in Section 6.0; changes made in Procedure

REVISION HISTORY

Rev. No.	CN No.	Effective Date	Description of Revision/CN
0		08/27/96	Initial Issue
0	TIP-CM-07-0-1	09/17/96	Text changes made for clarification; inclusion of previously omitted Appendix B; repagination. Affects Title Page, pages 3 through 7 of 7, and Appendices A and B.
0	TIP-CM-07-0-2	04/04/97	Addition of balance to acceptable list in Section 6.0; changes made in Procedure. Affects Title Page and pages 6 and 7 of 7.

Approved by: W. R. Lukens — 4/8/97
CRWMS LLNL Manager — Date

Approved by: Carol A. Brumburger for Bruce McNKS — 4/3/97
M&O LLNL Quality Assurance Manager — Date

Approved by: R. Daniel McCright — 3 April 1997
Technical Area Leader — Date

1.0 PURPOSE

This procedure describes the formulation and make-up of Simulated Concentrated Water (SCW), a high-ionic-content water to be used for Activity E-20-50 "Long-Term Corrosion Studies." This water has an ionic content which is nominally a factor of a thousand higher than that of "representative" waters at or near Yucca Mountain. "Representative" waters were chosen as J-13 well water [Harrar, 1990] and "perched" water at Yucca Mountain [Glassley, 1996] (see Table 1). J-13 well water is obtained from ground water that is in contact with the Topopah Spring tuff, which is the repository horizon rock. The "perched" water is located in the Topopah Spring tuff, but below the repository horizon and above the water table. A nominal thousand times higher ionic content was chosen to simulate the water that would result from the wetting of salts which have been previously deposited on a container surface.

The expected composition of the SCW is given in Table 1. It is anticipated that the actual composition of test solutions will be within ± 20% of these values. The changes in the corrosive properties of the test solutions will be acceptable within these values. In addition similar type materials are tested in the same test vessel, so minor vessel to vessel variation of solution composition is of limited significance.

Both of the "representative" waters have similar corrosive characteristics. The solution pH's and the concentrations of the aggressive anions (Cl^-, F^-, and SO_4^{2-}) are essentially equivalent from a corrosion stand point.

This aqueous solution is one of the four aqueous test solutions to be used in the activity. The other aqueous solutions included a Simulated Dilute Water (SDW), a simulated acidic concentrated water (SAW), and a simulated basic concentrated water (SBW).

This TIP documents the chemical reagents, reactant air, and the procedures used to make-up the aqueous solution for Activity E-20-50. More than 12,000 liters (3,170 gallons) of Simulated Concentrated Water solution are required for the test vessels for implementation of the full test matrix of the activity plan.

2.0 SCOPE

This procedure applies to the Simulated Concentrated Water solution, one of the aqueous solutions that are to be used in the test vessels for Activity E-20-50 "Long-Term Corrosion Studies."

3.0 RESPONSIBILITIES

The Principal Investigator (PI) or designee is responsible for:

- the conduct of the activities and methods described in this procedure, and
- maintaining laboratory scientific notebooks.

The Task Area Leader (TAL) is responsible for:

- ensuring that the requirements of this procedure are implemented,
- ensuring that personnel conducting the work are qualified and are trained to this procedure,
- verifying that this procedure meets the objectives of the Scientific Investigation Plan (SIP) "Metal Barrier Selection and Testing" (SIP-CM-01, Rev.3, WBS # 1.2.2.5.1) and Activity E-20-50 "Long-Term Corrosion Studies", and
- ensuring approval of this procedure.

The YMP Quality Assurance Manager (QA Manager) is responsible for:

- monitoring the work to assure proper implementation of this procedure, and
- assuring its continued effectiveness.

4.0 COMPOSITION OF SCW AND REACTANT AIR

4.1 Aqueous Solution Composition

The Simulated Concentrated Water (SCW) has a ionic composition that is nominally a factor of a thousand higher than that of "representative" water of Yucca Mountain. "Representative" waters were chosen J-13 well water [Harrar, 1990] and "perched" water at Yucca Mountain [Glassley, 1996]. J-13 well water is obtained from ground water that is in contact with the Topopah Spring tuff, which is the repository horizon rock. The "perched" water is located in the Topopah Spring tuff, but below the repository horizon and above the water table. The thousand times higher ionic content was chosen to simulate the water that may result from wetting of salts and minerals that have been deposited on the container surfaces.

The composition of J-13 well water and the "perched" water are given in Table 1. Only ions with concentration greater than 0.5 ppm are included in this table. Minor constituents have been detected in J-13 well water; these include Li, B, Al, Mn, Fe, Sr, and PO_4^{3-} ions. These constituents have been reported in the 10-100 µg/liter concentration. The most consistently determined minor constituents are Li and B at mean (several studies) concentrations of 48 and 134 µg/liter, respectively. The minor constituents are not explicitly included in the SCW. However, the reagent chemicals have some impurites, which may include the above noted impurities. **The minor constituents at the reported concentrations are not expected to significantly effect the corrosion of the test specimens.**

It is worth noting the differences in the "representative" waters. In terms of the calcium and bicarbonate concentrations, the "perched" water is higher in both of these constituents, and has a higher pH; these both are probably due to contact with calcium carbonate ($CaCO_3$) minerals. The concentrations of Na^+, K^+, F^-, and NO_3^- are slightly higher in J-13 well water.

Table 1. Compositions of "representative" Yucca Mountain waters J-13 well water and "perched" water, and the estimated composition of the simulated concentrated water.

Constituent	J-13 (mg/l) (mg/l)	"Perched" (mg/l)	Simulated Concentrated Water (estimated)
Na	45.80	36	40,900
Si	28.5	37	27 (60C); 49 (90C)
Ca	13.0	25	< 1
K	5.04	1.7	3,400
Mg	2.01	2.2	< 1
F^-	2.18	0.7	1,400
Cl^-	7.14	6.3	6,700
NO_3^-	8.78	4	6,400
SO_4^{2-}	18.4	15	16,700
HCO_3^-	128.9	147	70,000
$CaCO_3$	—	—	47,500 (precipitate)
$MgCO_3$			7,300 (precipitate)
pH	7.41	8.1	

The following paragraphs explain the reasoning used to arrive at the composition and formulation of the SCW. The silica content is based on solubility of α- cristobalite which is believed to be the dominant soluble silica phase of Yucca Mountain rock at 60 and 90°C [Wolery, 1983; Knauss, 1987]. Silica may be added to the solution by dissolution of sodium silicate. The salts, in general, are concentrated by a factor of a thousand over an "average" of the "representative" Yucca Mountain waters. The exceptions are calcium (Ca^{2+}), magnesium (Mg^{2+}), and bicarbonate (HCO_3^-), which are all at lower concentration.

Previous studies have indicated that extensive concentrating of water with relative ionic concentrations like those of the "representative" water (high bicarbonate) results in the precipitation of calcium and magnesium carbonates and silica-base minerals [Drever, 1982]. Calcite ($CaCO_3$) will precipitate first, with some magnesite ($MgCO_3$) co-precipitating in the calcite. The remaining magnesium will precipitate in silica-based minerals.

Simulations of concentrating the "representative" waters were run using the computer program "Geochemist's Workbend, Release 2.2" [Bethke, 1994]. The results generated were in agreement with the qualitative predictions based on the general solution composition. All of the calcium and magnesium was effectively precipitated during concentrating of the solution; a few ppm of each remained in solution.

The estimated composition of the SCW is given in Table 1. It is expected that the actual composition of test solutions will be within ± 20% of these values. The changes in the corrosive properties of the test solutions within these values will not be significant. In addition similar type materials are tested in the same test vessel, so minor vessel-to-vessel variation of solution composition is of limited significance.

4.2 Reactant Air

Reactant air is compressed building air which has been purified to remove hydrocarbons and water. Air will be purified by flowing through a Whatman Zero Air Generator (see Section 6.0). Nominal flow rates through each test vessel will be 200 ml/min. Air will exit through a condenser to remove water; this greatly reduces the amount of water loss from the test vessels.

Reactant air serves two purposes: 1) it keeps the oxygen content of the vessels constant, and 2) the slightly pressurized test vessel will keep the potentially contaminated room air out of the test vessels.

5.0 REAGENTS AND FORMULATION

5.1 Reagent Chemicals

In order to obtain the solution composition given in Table 1, various combinations of chemicals can be used. A spreadsheet has been developed which calculates the composition of a solution based on the added chemicals. **Copies** of typical outputs of the spreadsheets **are** shown in Appendix A **for 60 and 90°C solutions; the amount of silica changes with temperature**. Many of the chemicals listed in the spreadsheet are not used in this particular example. The inclusion of numerous chemicals in the spreadsheet allows the user the freedom to choose the needed chemicals based on availability, cost, and personal preference.

The algorithm to arrive at reagent concentrations was a trial and error method. The quantities of reagents required was estimated, and the spreadsheet calculated the total ionic content of the theoretical solution. Iteration was continued until an acceptable match was achieved.

A few guidelines were used in choosing the reagents. The choices for bicarbonate ions **were** $NaHCO_3$ **or** $KHCO_3$, since **these are** the common commercial source of bicarbonate. The use of potentially hazardous materials such as HF, MgF_2, and CaF_2 was avoided. The more soluble salts (minerals) were chosen, for example, magnesium sulfate was chosen over the less soluble carbonate and nitrate salts.

Also solution silica will be obtained by the addition of sodium silicate. (Calculations showed that dissolution of solid silica phases would take extended periods of time (>1000 days) in order for sufficient amounts of silica to dissolve.) Note using sodium silicate will result in slightly elevated sodium concentrations.

Using sodium silicate will result in the formation of hydroxyls equal to the number of moles of sodium atoms added. **In order to neutralize the hydroxyls, an equal number of moles of acid (hydrochloric, nitric, or sulfuric) will be added.**

Since a large percentage of both the calcium and magnesium will form carbonate precipitates, it was not necessary to add soluble salts of these ions to the level of the concentrating. However excess of these ions will be added such that precipitates of calcite and magnesite will form.

A word of caution in using the spreadsheet: the calculations assume that the chemicals dissolve completely and may therefore over estimate the composition of some species. The user must therefore be aware of potential solubility problems. A listing of the solubilities of various chemical is shown in Appendix B.

A typical example of chemicals used to make-up of the aqueous solution are listed in Table 2 along with the quantities required per 1000 l of solution.

Table 2. An example of the reagents and quantites required per 1000 liters of simulated aqueous solution.

Reagent	Quantity @ 60°C (gms / 1000 liters)	**Qualtity @ 90°C (gms / 1000 liters)**
$NaHCO_3$	**128,450.0**	**128,297.0**
NaF	**3,182.6**	**3,182.6**
Na_2SO_4	**12,236.4**	**12,254.5**
$Na_2SiO_3 \cdot 5H_2O$	**204.0**	**370.0**
$MgSO_4 \cdot 7H_2O$	**21,392.0**	**21,392.0**
$CaCl_2 \cdot 2H_2O$	**7,598.0**	**7,598.0**
$Ca(NO_3)_2 \cdot 4H_2O$	**12,168.5**	**12,168.5**
HCl	**3.73**	**70.1**
KCl	**6,417.8**	**6,282.0**
$KHCO_3$	**10.4**	**192.5**
$CaCO_3$	**37,117.3**	**37,117.3**
H_2SO_4	**89.3**	**76.79**

The chemicals and the quantities used in making up the test solutions will be listed in the Scientific Notebook or electronic media.

5.2 Purified Water

The make up of the test solutions requires large quantities of low ionic content water is required. The use of LLNL de-ionized water is acceptable. This water has an ionic content typically less than 1 ppm. This is less than 0.001% of the ionic content due to the added chemicals. The source of the water used in testing will be recorded in the scientific notebook.

5.3 Reactant Gas

The reactant air will be purified before entering the test vessels.

6.0 EQUIPMENT

A balance that can measure to 0.1 grams is acceptable for make-up of the test solutions. An acceptable balance is:

Mettler Balance Model # AT200
Serial Number 1114463500

Mettler Balance Model # PC16
Serial Number A51361

An air purifier for cleaning the building compressed air is required. The following unit or equivalent is acceptable:

Whatmann Type 76-818NA Zero Air Generator
Unit Serial Number 768180065B
Tower Module Serial Number 76811-10116B

This air purifier removes hydrocarbon to 0.1 ppm.

7.0 PROCEDURE

The following procedure will be followed in making-up of the Simulated Concentrated Water solutions for the test vessels:

1) Purified water is emplaced in the cleaned vessel; the liquid level is slightly less than the required depth for testing. (Need to account for rise in water level due to the specimens and racks, and the density decrease due to raising the water temperature to the test temperature.)

2) The amount of purified water added to the test vessels is estimated.

3) The required amounts of reagent chemicals is determined and entered in the scientific notebook or electronic media.

4) The purified water is heated to a nominal temperature of 40°C. This will accelerate reactions that occur in solution.

5) The water will be stirred. The stirrer mounted on the vessel is sufficient.

6) **Add chemicals to water. No particular order is required for chemical additions except that sulfuric acid will be the last chemical added to the test vessel.**

7) **Concentrated sulfuric acid shall be diluted 500-1000 times the required volume using deionized water and then added to the test vessel.**

8) **The vessel is sealed and brought to testing temperature for at least 24 hours.**

9) **The specimen racks are inserted into test vessel.**

10) **A sample of the test solution is withdrawn for analysis approximately a day after the level of water reaches the normal operation set point.**

Note: The liquid level in the test vessels will self-adjust to the required level. If the liquid level is low, the liquid level control system will add purified water. If the liquid level is high, water removal by the air purge will occur; this may be slow but it will occur. It is preferred to add water rather than to remove water, since the control system shuts down the heaters when the liquid level is above a certain height.

8.0 QA RECORDS

Any data that is pertinent to this TIP shall be entered into the Scientific Notebook or electronic media for Activity E-20-50. This shall include, but is not be limited to the chemical used lot # manufacturer supplied analysis, and actual reagent chemical amounts used for make-up.

9.0 REFERENCES

C.M. Bethke, The Geochemist's Workbench, Version 2.0; A Users Guide to Rxn, Tact, React, and Gtplot, Hydrogeology Program, University of Illinois, 1994.

J.I. Drever, The Geochemistry of Natural Waters, Prentice-Hall, Inc., Englewood Cliffs, NJ, 1982.

W. Glassley, private communication, 1996.

J.E. Harrar, J.F. Carley, W.F. Isherwood, and E. Raber, "Report of the Committee to review the Use of J-13 Well Water in Nevada Nuclear Waste Storage Investigations," Lawrence Livermore National Laboratory report UCID-21867, Livermore California, January 1990.

K.G. Knauss, W.J. Beiriger, D.W. Peifer, "Hydrothermal Interaction of Solic Wafers of Topopah Spring Tuff with J-13 Water at 90 and 150°C Using Dickson-Type, Gold-Bag Rocking Autoclaves: Long-Term Experiments," Lawrence Livermore National Laboratory Report UCRL-53722, May 1987.

T.J. Wolery, Memo GCC-83-3/1773w, "Summary of Silica Solubilty Data for Acid-to-Neutral pH Conditions," 16 Nov. 1983.

Compound	Mol Wt.	gms/ 1000 l	K	Na	Mg	Ca	Cl	F	HCO3	CO3	SO4	NO3	SiO3	H
NaCl	58.44	0.0		0.0			0.0							
NaOH	40.00	0.0		0.0										
NaHCO3	84.01	128450.0		35152.3					93297.7					
Na2CO3	105.99	0.0		0.0						0.0				
Na2SO4	142.04	12236.4		3961.0							8275.4			
NaNO3	84.99	0.0		0.0								0.0		
Na2CO3	105.99	0.0		0.0						0.0				
NaF	41.99	3182.6		1742.6				1440.0						
Na2SiO3•9H2O	284.20	0.0		0.0									0.0	
Na2SiO3•5H2O	212.14	204.0		44.2									73.2	
MgCl2•6H2O	203.31	0.0			0.0		0.0							
MgF2	62.31	0.0			0.0			0.0						
MgSO4	120.37	0.0			0.0						0.0			
MgSO4•7H2O	246.48	21392.0			2110.0						8337.2			
Mg(NO3)2•6H2O	256.41	0.0			0.0							0.0		
CaCl2	110.99	0.0				0.0	0.0							
CaCl2•2H2O	147.02	7598.0				2071.4	3664.5							
CaF2	78.08	0.0				0.0		0.0						
CaCO3	100.09	37117.3				14863.3				22254.0				
CaSO4	136.14	0.0				0.0					0.0			
CaSO4•2H2O	172.17	0.0				0.0					0.0			
Ca(NO3)2•4H2O	236.15	12168.5				2065.3						6390.0		
CaCO3MgCO3	184.41	0.0			0.0	0.0				0.0				
H2SO4	98.08	89.3000									87.5			1.8355
HCl	36.46	3.7280					3.6							0.1031
HNO3	63.01	0.0										0.0		0.0000
KF•2H2O	94.13	0.0	0.0					0.0						
KCl	74.56	6417.8	3366.0				3051.8							
K2SO4	174.27	0.0	0.0								0.0			
KNO3	101.11	0.0	0.0									0.0		
KHCO3	100.12	10.4	4.1						6.3					
K2CO3	138.21	0.0	0.0							0.0				
KOH	56.11	0.0	0.0											
Totals			3370.0	40900.0	2110.0	19000.0	6720.0	1440.0	93304.1	44507.9	16700.0	6390.0	73.2 27.0	1.9386
Target			3370.0	40900.0	2110.0	19000.0	6720.0	1440.0	137950.0		16700.0	6390.0	27 (Si)	1.9386
										137812				
						[HCO3] + [CO3] + [OH] = 1379.5								

Compound	Mol Wt.	gms/ 1000 l	K	Na	Mg	Ca	Cl	F	HCO3	CO3	SO4	NO3	SiO3	H
NaCl	58.44	0.0		0.0			0.0							
NaOH	40.00	0.0		0.0										
NaHCO3	84.01	128297.0		35110.4					93186.6					
Na2CO3	105.99	0.0		0.0						0.0				
Na2SO4	142.04	12254.5		3966.9							8287.6			
NaNO3	84.99	0.0		0.0								0.0		
Na2CO3	105.99	0.0		0.0						0.0				
NaF	41.99	3182.6		1742.6				1440.0						
Na2SiO3•9H2O	284.20	0.0		0.0									0.0	
Na2SiO3•5H2O	212.14	370.0		80.2									132.7	
MgCl2•6H2O	203.31	0.0			0.0		0.0							
MgF2	62.31	0.0			0.0			0.0						
(MgCO3)4•Mg(	485.69	0.0			0.0					0.0				
MgSO4	120.37	0.0			0.0						0.0			
MgSO4•7H2O	246.48	21392.0			2110.0						8337.2			
Mg(NO3)2•6H2	256.41	0.0			0.0							0.0		
CaCl2	110.99	0.0				0.0	0.0							
CaCl2•2H2O	147.02	7598.0				2071.4	3664.5							
CaF2	78.08	0.0				0.0		0.0						
CaCO3	100.09	37117.3				14863.3				22254.0				
CaSO4	136.14	0.0				0.0					0.0			
CaSO4•2H2O	172.17	0.0				0.0					0.0			
Ca(NO3)2•4H2	236.15	12168.5				2065.3						6390.0		
CaCO3MgCO3	184.41	0.0			0.0	0.0				0.0				
H2SO4	98.08	76.790									75.2			1.578
HCl	36.46	70.100					68.2							1.938
HNO3	63.01	0.0										0.0		0.000
KF•2H2O	94.13	0.0	0.0					0.0						
KCl	74.56	6282.2	3294.8				2987.4							
K2SO4	174.27	0.0	0.0								0.0			
KNO3	101.11	0.0	0.0									0.0		
KHCO3	100.12	192.5	75.2						117.3					
K2CO3	138.21	0.0	0.0							0.0				
KOH	56.11	0.0	0.0											
													132.7	
Totals			3370.0	40900.0	2110.0	19000.0	6720.0	1440.0	93303.9	44507.9	16700.0	6390.0	49.0	3.516
Target			3370.0	40900.0	2110.0	19000.0	6720.0	1440.0	137950.0		16700.0	6390.0	49 (Si)	3.516
										137812				
						[HCO3] + [CO3] + [OH] = 1379.5								

Appendix B. Solubilites in Water

Compound	Formula		Mol Wt.	Solubility gms/100cc	Solubiliy mg / l	T(°C)	Solubility gms/100cc	Solubiliy mg/l	T(°C)
Calcium sulfate	CaSO4	nat anhydrite	136.14	0.2090	2090	30	0.1619	1619	100
Calsium sulfate dihydrate	CaSO4•H20	nat gypsum	172.17	0.2410	2410		0.222	2220	100
Calcium nitrate	Ca(NO3)2		164.09	121.2000	1E+06	18	376	3760000	100
Calcium Chloride	CaCl2		110.99	74.5000	745000	20	159	1590000	100
Calcium Flouride	CaF2	nat flouride	78.08	0.0016	16	18	0.0017	17	26
Calcium Carbonate	CaCO3	calcite	100.09	0.0014	14	25	0.0018	18	75
Calcium hydroxide	Ca(OH)2		74.09	0.1850	1850	0	0.077	770	100
Sodium sulfate	Na2SO4	nat thenardite	142.04	4.7600	47600	0	42.7	427000	100
Sodium nitrate	NaNO3	soda niter	84.99	92.1000	921000	25	180	1800000	100
Sodium Chloride	NaCl	halite	58.44	35.7000	357000	0	39.12	391200	100
Sodium Flouride	NaF	nat villiaumite	41.99	4.2200	42200	18		0	
Sodium carbonate	Na2CO3		105.99	7.1000	71000	0	45.5	455000	100
Sodium Bicarbonate	NaHCO3		84	6.9000	69000	0	16.4	164000	60
Sodium hydroxide	NaOH		40	42.0000	420000	0	347	3470000	100
Sodium Silicate	Na2SiO3	metasilicate	122.06	soluble		-	soluble; dissolves		-
Magnesium sulfate	MgSO4		120.37	26.0000	260000	0	73.8	738000	100
Magnesium nitrate	Mg(NO3)2•6H2O		256.41	124.0000	1E+06		vs		
Magnesium chloride	MgCl2		95.22	54.2500	542500	20	72.7	727000	100
Magnesium flouride	MgF2	nat sellaite	62.31	0.0076	76	18	i		
Magnesium carbonate	MgCO3	nat magnesite	84.32	0.0106	106			0	
Magnesium carbonate trihydrate	3MgCO3•Mg(OH)	nat hydromag	365.34	0.0400	400		0.011	110	
Magnesium carbonate basic	MgCO3•3H2O	nat nesqueho	138.37	0.179	1790	16	d		
Magnesium hydroxide	Mg(OH)2	nat brucite	58.33	0.0009	9	18	0.004	40	100
Potassium sulfate	K2SO4	nat arcanite	174.27	12	120000	25	24.1	241000	100
Potassium sulfate, hydrogen	KHSO4	nat mercallite	136.17	36.3	363000	0	121.6	1216000	100
Potassium nitrate	KNO3	saltpeter	101.11	13.3	133000	0	247	2470000	100
Potassium chloride	KCl	nat sylvite	74.56	23.8	238000	20	56.7	567000	100
Potassium flouride	KF		58.1	92.3	923000	18	vs		
Potassium carbonate	K2CO3		138.21	112	1E+06	20	156	1560000	100
Potassium Carbonate, hydrogen	KHCO3		100.12	22.4	224000		60	600000	60
Potasssium Hydroxide	KOH		56.11	107	1E+06	15	178	1780000	100

Source: CRC Handbook of Chemistry and Physics, R.C. Weast, M.J. Astle, eds., CRC Press, Inc., Boca Raton, FL, 1981.